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Production and analysis of bio-diesel from non-edible oils—A review

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Abstract

Bio-diesel has become more attractive recently because of its environmental benefits and it is derived from renewable resources, bio degradable and non-toxic in nature. Several bio-diesel production methods have been developed, among which transesterification using alkali catalyst gives high level of conversion of triglycerides to their corresponding methyl ester in short reaction time. The process of transesterification is affected by the reaction condition, molar ratio of alcohol to oil, type of alcohol, type and amount of catalysts, reaction time and temperature, purity of reactants free fatty acids and water content of oils or fats. In this work, an attempt has been made on review of bio-diesel production, methods of analyzing, bio-diesel standard, resources available, process developed performance in internal combustion engines, teardown analysis of bio-diesel B20 operated vehicle, recommendation for development of bio-fuels, environmental considerations, economic aspects and advantages. The technical tools and process for monitoring the transesterification reaction like TLC, GC, HPLC, GPC, ^{1}H NMR and NIR have also been summarized in this paper.

Keywords: Triglycerides; Transesterification; Methyl esters; Reaction condition

Contents

Abbreviations: Na, sodium; K, potassium; CO_2, carbon dioxide; CO, carbon monoxide; HC, hydro carbon; SO_2, sulphur dioxide; NO_x, nitrogen oxides; PAH, poly aromatic hydro carbon; NaOH, sodium hydroxide; NaOME, sodium methoxide; KOH, potassium hydroxide; KOME, potassium methoxide; H_2SO_4, sulphuric acid; H_3PO_4, phosphoric acid; HCI, hydrochloric acid; GC, gas chromatography; TLC, thin layer chromatography; FID, flame ionization detection; HPLC, high performance liquid chromatography; GPC, gel permeation chromatography; MSD, mass spectrometric detector; HPLC-PAD, high performance liquid chromatography-pulsed amperometric detection; THF, tetrahydrofuran; ^{1}H NMR, proton nuclear magnetic resonance; NIR, near infra red; CFPP, cold filter plugging point.

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1. Introduction

1.1. Background

Majority of the world's energy needs are supplied through petrochemical sources, coal and natural gases, with the exception of hydroelectricity and nuclear energy, all these sources are finite and at current usage rates will be consumed shortly [1]. Diesel fuel have an essential function in the industrial economy of a developing country and are used in transports, industrial and agricultural goods, etc. Compared to the rest of the world, India's demand for diesel fuels is six times that of gasoline. The consumption of diesel fuels in India in 1994–1995 was 28.30 million tonnes of diesel and 40.34 million tonnes of diesel in 2000–2001, which was 43.2% of the total consumption of petroleum products [2]. Economic growth is always accompanied by commensurate increase in the transport. This has stimulated the recent interest in alternative sources for petroleum-based fuels. An alternative fuel should be easily available, environment friendly and techno-economically competitive. One of such fuels is triglycerides and their derivatives. Vegetable oils, being renewable, are widely available from a variety of sources and have low sulphur contents close to zero and hence cause less environmental damage (lower green house effect) than diesel. Chemically the oils consist of triglyceride molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids differ by the length of carbon chain, orientation and position of double bonds in these chains. Thus bio-diesel refers to lower alkyl esters of long chain fatty acids, which are synthesized either by transesterification with lower alcohols or by esterification of fatty acids.

1.2. Triglycerides as diesel fuel

The use of vegetable oils, such as soya-bean, palm, sunflower, peanut and olive oil as alternative fuel has been around for 100 years when the inventor of the diesel engine Rudolph Diesel first tested peanut oil, in his compression ignition engine [3,4]. Different countries are looking for different types of vegetable oils as substitutes for diesel fuels that depending upon the climate and soil conditions. For example, soya-bean oil in U.S., Rapeseed and Sunflower oils in Europe, palm oil in Southeast Asia and Coconut oil in Philippines are being used. The use of vegetable oils as sources of diesel would require more efforts to increase the production of oil seed and to develop new and more productive plant species with high yield of oil. Besides, some species of plants yielding non-edible oils. The planning commission of India has launched a bio-fuel project in 200 districts of the 18 states in India. It has recommended two plant species viz. Jatropha (Jatropha curcas) and Karanj (Pungamia pinnata) for bio-diesel production [5–7]. Both these plants may be grown on a massive scale on agricultural/degraded/waste lands, so that the chief resource may be available to produce bio-diesel on 'farm scale'.

Vegetable oils occupy a prominent position in the development of alternative fuels although, there have been many problems associated with using it directly in diesel engine. These includes:

1. High viscosity of vegetable oil interferes with the injection process and leads to poor fuel atomization.
2. The inefficient mixing of oil with air contributes to incomplete combustion, leading to high smoke emission.
3. The high flash point attributes to lower volatility characteristics.
4. Lube oil dilution.
5. High carbon deposits.
6. Ring sticking.
7. Scuffing of the engine liner.
8. Injection nozzle failure.
9. Types and grade of oil and local climatic conditions.

10. Both cloud and pour points are significantly higher than that of diesel fuel. These high values may cause problems during cold weather.

These problems are associated with large triglycerides molecule and its higher molecular mass, which is avoided by chemically modified to vegetable oil in to bio-diesel that is similar in characteristics of diesel fuel [8–10].

1.3. Bio-diesel

The plant oils usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Because of these the oil cannot be used as fuel directly. To overcome these problem the oil requires slight chemical modification mainly transesterification, pyrolysis and emulsification. Among these, the transesterfication is an important process to produce the cleaner and environmentally safe fuel from vegetable oils.

Bio-diesel is defined as the mono alkyl esters of long chain fatty acids derived from renewable feed stock, such as vegetable oil or animal fats, for use in compression ignition engines [4]. Bio-diesel which is considered as a possible substitute of conventional diesel fuel is commonly composed of fatty acid methyl/ethyl esters, obtained from triglycerides by transesterification with methanol/ethanol respectively. Bio-diesel is compatible with convention diesel and both can be blended in any proportion.

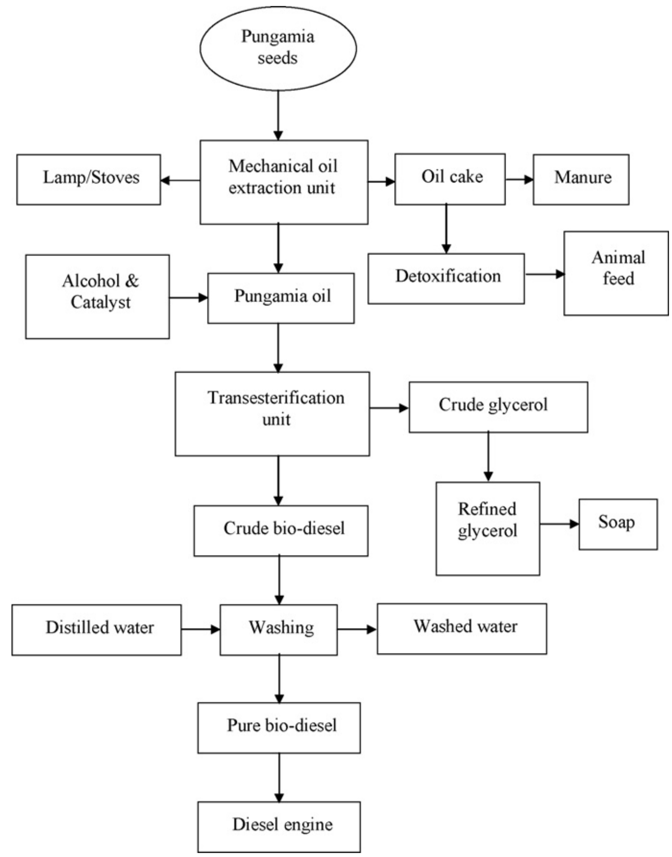


Fig. 1. Process flow chart for bio-diesel production.

2. Process of bio-diesel production

2.1. Transesterification reaction

Transesterification [11] also called alcoholysis is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis except that an alcohol is used instead of water [1]. This has been widely used to reduce the viscosity of the triglycerides. The transesterification is represented as:

$$\underset{\text{Ester}}{RCOOR'} + \underset{\text{Alcohol}}{R''OH} \rightleftharpoons \underset{\text{Ester}}{R'COOR''} + \underset{\text{Alcohol}}{ROH} \qquad (1)$$

Equation 1. Transesterification process

If methanol is used in this process then it is called methanolysis. Methanolysis of triglycerides represented in Eq. (2).

$$\begin{array}{lcclcl} CH_2\text{-}COOR^1 & & & CH_2OH & & R^1COOCH_3 \\ | & & & | & & + \\ CH\text{-}COOR^2 & +3CH_3OH & \rightleftharpoons & CH\ OH & + & R^2COOCH_3 \\ | & & & | & & + \\ CH_2\text{-}COOR^3 & & & CH_2OH & & R^3COOCH_3 \\ \text{Vegetable oil} & \text{Alcohol} & & \text{Glycerol} & & \text{Methyl-ester} \end{array} \qquad (2)$$

Equation 2. Methanolysis of Tri-glycerides

Transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants. However, the presence of a catalyst (a strong acid or base) accelerates the conversion.

2.2. Chemistry of transesterification process

The overall transesterification reaction is given by Eq. (2). However, three consecutive and reversible reactions are believed to occur. These reactions are represented in Eq. (3). The process flow chart for bio-diesel production from pungamia oil is shown in Fig. 1.

$$\begin{array}{l} \text{Triglycerides} + ROH \rightleftharpoons \text{Diglycerides} + R^1COOR \\ \text{Diglycerides} + ROH \rightleftharpoons \text{Monoglycerides} + R^2COOR \\ \text{Monoglycerides} + ROH \rightleftharpoons \text{Glycerol} + R^3COOR \end{array} \qquad (3)$$

Equation 3 Chemistry of transesterification

The first step in the conversion is triglycerides to diglycerides followed by the conversion of diglycerides to monoglycerides and of monoglycerides to glycerol yielding one methyl ester molecule from each glycerides at each step [12,13].

3. Variables affecting transesterification reaction

3.1. Effect of free fatty acids and moisture

The free fatty acid and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. To carry the base catalyzed reaction to complete; the three free fatty acid (FFA) value lower than 3% is needed. The higher the acidity of the oil, smaller is the conversion efficiency. Both, excess as well as insufficient amount of catalyst may cause soap formation [14]. The starting materials used for base catalyzed alcoholysis should meet certain specifications. The triglycerides should have lower acid value and all material should be substantially anhydrous. The addition of more sodium hydroxide catalyst compensates for higher acidity, but the resulting soap causes an increase in viscosity or formation of gel, that interferers in the reaction as well as with separation of glycerol [15]. When the reaction conditions do not meet the above requirements, ester yields are significantly reduced. The methoxide and hydroxide of Na and K should be maintained in anhydrous state, prolonged contact with air would diminish the effectiveness of these catalysts through interaction with moisture and CO_2.

3.2. Catalyst type and concentration

Catalyst used for the transesterification of triglycerides is classified as alkali, acid, enzyme or heterogeneous catalysts, among which alkali catalysts like NaOH, NaOMe, KOH and KOMe are more effective [16]. If the oil has high free acid content and more water, acid catalyst is suitable. The acids could be H_2SO_4, H_3PO_4 HCl or organic sulfonic acids. Methanolysis of beef tallow was studied with catalyst NaOH and NaOMe. Comparing the two catalysts, NaOH was significantly better than NaOMe [17]. Alkali metal alkoxides are most effective Transesterification catalyst compared to the acid catalyst. Sodium alkoxides are the mostly efficient catalysts, although KOH and NaOH can also be used. Transmethylation occurs approximately 4000 times faster in presence of an alkaline catalyst than the same amount of acidic catalyst [18]. As they are less corrosive to industrial equipments, alkaline catalysts are preferred in industrial processes. The concentration in the range of 0.5–1.0% (w/w) has found to yield 94–99% conversion of vegetable oils into ester and further increase of catalyst concentration does not affect the conversion but add to extra cost, as the catalyst needs to be removed from the reaction mixture after completion of reaction [19–21].

3.3. Molar ratio of alcohol to oil and type of alcohol

Another important variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The stoichiometry of the transesterification reaction required 3 mol of alcohol per mol of triglyceride to yield three mol of fatty ester and 1 mol of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. A molar ratio of 6:1 is normally used in industrial process because the yield of ester is higher than 98% by weight. The molar ratio has no affect on acid, peroxide, soaponification and iodine value of methyl esters [22]. However, the high molar ratio of alcohol to vegetable oil interferes with separation of glycerin because; there is an increase in solubility. When glycerin remains in solution, it helps drive the equilibrium to back to the left, lowering the yield of esters. The transesterification of Cynara oil with ethanol was studied at molar ratios between 3:1 and 15:1. The ester yield used as the molar ratio increased up to a value of 12:1. The best results were for molar ratios between 9:1 and 12:1. For molar ratios less than 6:1, the reaction was incomplete. For a molar ratio of 15:1 the separation of glycerin is difficult and the apparent yield of ester decreased because a part of the glycerol remains in the bio-diesel phase. Therefore molar ratio 9:1 seems to be the most approximate [23].

The base catalyzed formation of ethyl ester is difficult compared to the formation of methyl esters. In the case of methanolysis, formation of emulsions quickly and easily breaks down to form a lower glycerol rich layer and upper methyl ester rich layer. In ethanolysis, these emulsions are more stable and severely complicate the separation and purification of esters [15]. The emulsion are caused in part by formation of the intermediates, mono and diglycerides, which have both polar hydroxyl groups and non-polar HC chains. These intermediates are strong surface active agents. The requirements are the reaction to be as complete as possible, thereby reducing the concentrations of mono and diglycerides.

3.4. Effect of reaction time and temperature

The literature (Freedman et al. 1984) has revealed that the rate of reaction is strongly influenced by the temperature. However, given enough time, the reaction will proceed to near completion even at room temperature [18]. However, the reaction is conducted close to the boiling point of methanol (60–70 °C) at atmospheric pressure for a given time. Such mild reaction conditions require the removal of free fatty acids from the oil by refining or pre esterification. Therefore degummed and de acidified oil is used as feedstock [15]. Pre treatment is not required if the reaction is carried out under high pressure (9000 kPa) and high temperature (240 °C). Under these conditions simultaneous esterification and transesterification take place [24]. The maximum yield of esters occurs at a temperatures ranging from 60 to 80 °C at a molar ratio of (alcohol to oil) 6:1. Further increasing temperature, the yield of esters have a negative effect on the conversion [19,25].

3.5. Mixing intensity

Mixing is very important in the transesterification reaction, as oils or fats are immiscible with NaOH–MeOH solution. Once the two phase are mixed and the reaction is started stirring is no longer needed. Methanolysis was conducted with different rate of stirring such as, 180, 360 and 600 revolution per minute (rpm). The reaction is incomplete with 180 rpm and rate of mixing was insignificant for methanolysis. The yield of methyl

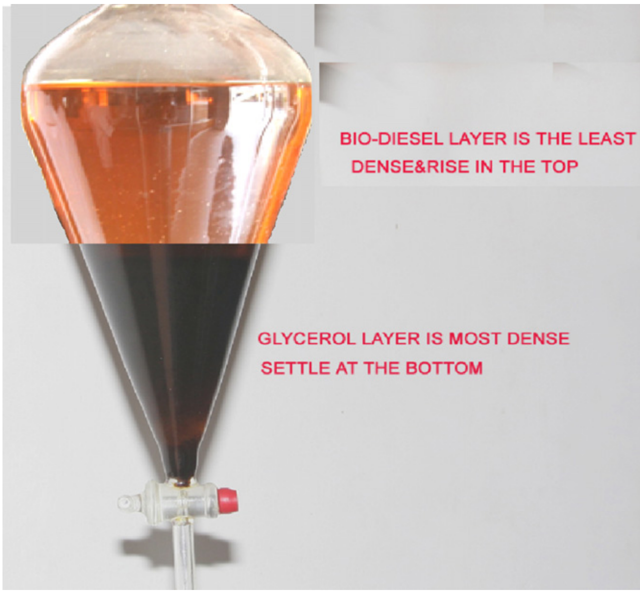


Fig. 2. Separation of glycerol from bio-diesel.

esters at 360 rpm and 600 rpm was same after 3 h of reaction [26]. Reaction time is the controlling factor for determining the yield of methyl esters. This suggested that the stirring speeds investigated exceeded the threshold requirement of mixing.

3.6. Separation of bio-diesel

Murugesan et al. [27] reported that, after completion of the reaction the product is kept for a certain time interval for separation (approx. 12 h) of bio-diesel & glycerol layer as shown in Fig. 2.

The mixture of KOH and methonal settles at the bottom of the funnel because of higher density compare with bio-diesel. Where as small amount of catalyst, methanol & glycerol are in the upper bio-diesel layer. The upper layer is collected for further purification by washing.

3.7. Washing of bio-diesel

Murugesan et al. [28] reported that, washing is a process to remove entrained glycerol, catalyst, soap & excess methanol. The excess methanol in bio-diesel corrodes the fuel injection system and hence it should be separated from the bio-diesel.

3.8. Bubble-washing and oxidation

Without oxygen the oil can't oxidise and polymerize. Everyone knows that a fish-tank aerator pump the water with oxygen so the fish can breathe. Bubble washing does the same thing to bio-diesel, pumping it with oxygen.

We are using a small air pump, usually an aquarium aerator pump with a bubble-stone. Water is added to the bio-diesel in the separating funnel (usually a quarter to a half as much water as bio-diesel). The water sinks to the bottom, throw in the bubble-stone, which also sinks to the bottom, and switch on the pump. Air bubbles (smaller size are best) rise through the water and into the bio-diesel, carrying a film of water around them, which washes the bio-diesel around the bubble as shown in Fig. 3. When it reaches the surface, the bubble burst, leaving the water to sink back down again, washing the fuel again.



Fig. 3. Bubble wash.

Usually three or four times the water wash is done with a time interval of one hour between each wash. After the water is settled it is removed via bottom-drain of the separating funnel and replaced with fresh water. The distilled water is used always for washing the bio-diesel to avoid the contamination of oil. The clear water settled at the bottom of the separation funnel and bio-diesel is formed at top layer as shown in Fig. 4.

3.9. Drying bio-diesel

Drying is ascertained by heating the washed fuel approximately to 110 °C in an open container until there is no more steam from in the fuel, which should be a clear, amber- colored liquid as shown in Fig. 5. This heating process will also drive off any traces of remaining alcohol as well. Then it is allowed to cool to room temperatures, it can be pumped directly into vehicles, or into storage containers.

If the fuel still appears somewhat cloudy after drying. The drying cycle should be repeated but the likely culprit is probably the presence of non-water soluble contaminants in the fuel (such as mono and Di-glycrides). The pure Bio-diesel is collected and stored in the separating funnel as shown in Fig. 6.

4. Quantification of methyl esters

Various analytical methods were developed for analyzing mixtures containing fatty acids esters and mono-, di-, and triglycerides obtained by the transesterification of vegetable oils.



Fig. 4. Pure bio-diesel at top layer & clear water at bottom layer.

Analysis were performed by a thin layer chromatography/flame ionization detector (TLC/FID). Steryl alcohol used as an internal standard. From plots of areas and weight ratios of methyl linoleate and mono-, di-, and tri-linolein, linear equations were developed from which response factors were calculated.

4.1. Gas chromatographic method (GC)

Gas chromatographic method for the simultaneous determination of glycerol, mono-, di-, and tri-glycerides in vegetable oil methyl esters has been developed. In principle, glycerol, mono-, di-, and tri-glycerides can be analyzed on highly inert-columns coated with a polar stationary phases without derivatization. The inertness of the column, required to obtain good peak shapes and satisfactory recovery, cannot be easily maintained in routine analysis. Most reports on the use of GC for bio-diesel analysis employ flame-ionization detectors (F1D), although the use of mass spectrometric detector (MSD) would eliminate any ambiguities about the nature of the electing materials. Since mass spectra unique to individual compounds would be obtained [29].

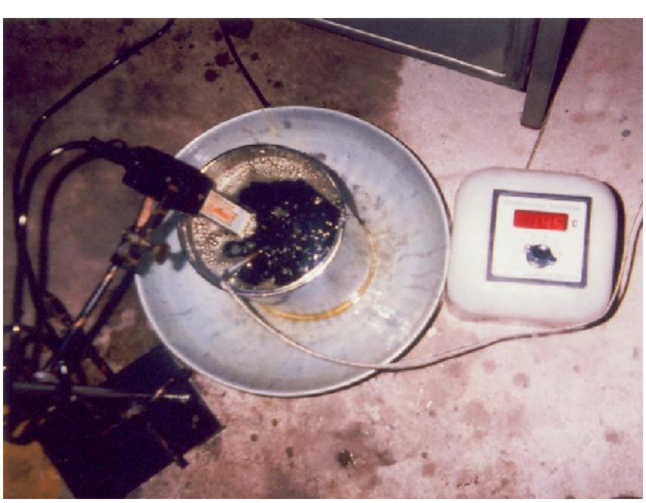


Fig. 5. Drying the bio-diesel in open container.



Fig. 6. Pure bio-diesel.

4.2. High performance liquid chromatography method (HPLC)

A general advantage of HPLC compared to GC is that time and reagent consuming dramatization are not necessary, which reduces analysis time. The first literature on HPLC method describes the determination of overall content of mono-, di-, and tri-glycerides in fatty acid methyl esters by iso-cratic liquid chromatography using a density detector. The separation was achieved by coupling a cyano-modified silica column with two GPC columns; Chloroform with an ethanol content of 0.6% is used as an eluent. This system allowed for the detection of mono-, di-, and tri-glycerides as well as methyl esters as classes of compounds. The system was useful for the study of degree of conversion of the transesterification reaction [30].

HPLC with pulsed amperometric detection (PAD) was used to determine the amount of free glycerol in vegetable oil esters. The HPLC–PAD method has proved to be simple, rapid and accurate [31]. The major advantage of this method is its high sensitivity. The simultaneous detection of residual alcohol is also possible with this technique [29]. HPLC equipped with a refractive index detector was used for the analysis of bio-diesel produced from soya-bean oil [13]. The HPLC mobile phases was consisted of acetone and acetonitrile. Mono-, di-, and tri-glycerides were quantified to study the reaction kinetics for transesterification.

Table 1
Bio-diesel standard table

Property	ASTM Method	Limits
Flash point (°C)	D93	130 minimum
Water & Sediment (vol%)	D2709	0.050 maximum
Kinematic Viscosity, 40 C (mm^2/s)	D445	1.9–6.0
Sulfated ash (% mass)	D874	0.020 maximum
Sulfur	D5453	–
S 15 Grade (ppm)	–	15 max
S 500 Grade	–	500 max
Copper Strip Corrosion	D130	No.3 maximum
Cetane	D613	47 minimum
Cloud Point (°C)	D2500	Report
Carbon residue 100% sample (% mass)	D4530*	0.050 maximum
Acid number (mg KOH/g)	D664	0.50 maximum
Free glycerin (% mass)	D6584	0.020 maximum
Total glycerin (% mass)	D6584	0.240 maximum
Phosphorus content (% mass)	D4951	0.001 maximum
Distillation temperature, atmospheric equivalent temperature, 90% recovered (°C)	D1160	360 maximum
Sodium/potassium (ppm)	UOP391	5 max combined

4.3. Gel permeation chromatography method (GPC)

A method for simultaneous analysis of transesterification reaction products mono-, di- and tri-glycerides, glycerol and methyl esters was developed using gel permeation chromatography coupled with refractive index detector [32]. The mobile phase was HPLC grade THF (Tetra Hydro Furan) at a flow rate of 0.5 ml/min at room temperature and the sample injection size was 10 macro lit. Sample preparation involves only dilution and neutralization. GPC was used to evaluate the influence of different variables affecting the transesterification of rapeseed oil with anhydrous ethanol and sodium ethoxide as catalyst [25]. GPC has made the quantization of ethyl esters, mono-, di-, and tri-glycerides and glycerol.

4.4. ^{1}H NMR method (proton nuclear magnetic resonance)

The yield of Transesterification reaction utilized ^{1}H NMR depicting its progressing spectrum [33]. The yield of methyl esters was calculated by comparing the peak area of methoxy and methylene protons.

4.5. NIR spectroscopy (near infra red)

NIR spectroscopy has been used to monitor the transesterification reaction [34]. The basis for quantization of the turn over from triglycerides feed stock to methyl ester product is differences in the NIR spectra of their classes of compounds. The mid range IR spectra of triglycerides and methyl esters of fatty acids are almost identical and offer no possibility for distinguishing.

5. Fuel properties and specification of bio-diesel

Since bio-diesel is produced in quite differently scaled plants from vegetables oils of varying origin and quality, it was necessary to install a standardization of fuel quality to guarantee engine performance without any difficulties. The parameters, which define the quality of bio-diesel, can be divided into two groups. One group contains general parameters, which are also used for mineral oil based fuel and the other group especially describes the chemical composition and purity of fatty acid alkyl esters [35].

Among the general parameters for bio-diesel the viscosity of fatty acid methyl esters can go very high levels and hence it is important to control it within an acceptable level to avoid negative impacts on fuel injectors system performance. Therefore viscosity specifications proposed are nearly same as that of the diesel fuel as shown in bio-diesel standard Table 1.

Flash point of a fuel is the temperature at which it will ignite when exposed to a flame. The flash point of bio-diesel is higher than the petro-diesel, which is safe for transport purpose.

Cold filter plugging point (CFPP) of a fuel reflects its cold weather performance. At low operating temperature, fuel may thicken and might not flow properly affecting the performance of fuel lines, fuel pumps and injectors. Normally either pour point or CFPP are specified.

Cetane number is indicative of its ignition characteristics. Higher the cetane number better it is in its ignition properties. Cetane number affects the engine performance parameters like combustion, stability, driveability, white smoke, noise and emissions of CO and HC. Bio-diesel has higher cetane number than conventional diesel fuel, which results in higher combustion efficiency.

Neutralization number is specified to ensure proper ageing properties of the fuel. It reflects the presence of free fatty acids. Carbon residue of the fuel is indicative of carbon depositing tendencies of the fuel. Canradsons carbon residue for bio-diesel is more important than that in diesel fuel because it shows a high correlation with presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities. The presence of high level of alcohol in bio-diesel cause accelerated deterioration of natural rubber

seals and gaskets. Therefore, control of alcohol content is required.

6. Performance of bio-diesel in diesel engine

Conventional Internal Combustion Engines can be operated with bio-diesel without major modification [36]. In comparison to diesel, the higher cetane number of bio-diesel results in shorter ignition delay and longer combustion duration and hence results in low particulate emissions and minimum carbon deposits on injector nozzles. It is reported that if an engine is operated on bio-diesel for a long time, the injection timing may be required to be readjusted for achieving better thermal efficiency [37,38]. Various blends of bio-diesel with diesel have been tried, but B-20 (20% bio-diesel + 80% diesel) has been found to be the most approximate blend. Further studies have revealed that bio-diesel blends lead to a reduction in smoke opacity, and emissions of particulates, unburnt HCS, CO_2 and CO, but cause slightly increase in nitrogen oxides emission [39]. All the blends have a higher thermal efficiency than diesel and so give improved performance. A concentration of 20% bio-diesel gave maximum improvement in peak thermal efficiency, minimum break specific energy consumption and minimum smoke opacity. Hence, B-20 was recommended as the optimum blend for long-term engine operation [38].

7. Teardown analysis

Fraer et al. [40] reported that 1996, Mack MR 688p model vehicle having six cylinders its compression ratio of 16.5:1 and producing the power 300 hp at 1950 rpm used in postal purposes. The engine and fuel system components were disassembled, inspected and evaluated to compare wear characteristics after 4 years of operation and more than 6,00,000 miles accumulation on B 20 no difference in wear or other issues were noted during the engine teardown. The cylinder heads of B20 engines contained a heavy amount of sludge around the rocker assemblies that was not found in the diesel engines. The sludge contained high levels of sodium possibly caused by accumulation of soaps in the engine oil. The B20 engines required injector nozzle replacement over the evaluation and teardown period this is due to out of specification of fuel. The biological contaminants may have causes the filter plugging.

8. Recommendation for development of bio fuels [41]

- As the stock of fossil fuel is getting depleted, emphasis should be given to renewable sources of fuel such as Bio-Fuel crops and tree brone oilseeds.
- DST funding is required for land resources management water resources, mineral, fossil fuels.
- Design, develop and popularize appliances and equipments specifically for rural application.
- Prima facie, bio-diesel seems to have significant potential to contribute to Indian's energy security, the need of the hour is to under take R&D on sustainable plantation management, oil extraction and use environmental and social impact assessment and build institutional models.
- To develop fuel wood and bio-diesel plantation to reduce drudery in collecting fuel wood for meeting house hold energy equipment.
- A common plate form for interaction with farmers extension personnel, researchers and technologists with media personnel must be created.
- Contact training programmers to sensitize media personnel on latest technologies and developments related to rural development.
- Creating awareness regarding loan, insurance facilities subsidies, etc.

8.1. Need for a policy initiative [42]

- Initiate dialogue on classification of non-edible vegetable oils based on their origin and practices, from that of natural forest/social forestry/avenue plantations.
- Cultivated vegetable oils can be dedicated/diverted to agricultural operations to source energy requirements.
- Tree borne oils of forest origin can go for central pool for blending as a transportation fuel.
- Need for a long term National Policy on utilization of these oils as per their allocations.
- Sustain this concept till it is socially reproduced, and becomes an agricultural activity by the farmers.
- Energy recovery from de-oiled cakes is encouraged as an on farm activity, for fertilizer, and for duel fuel mode engine applications.
- Arriving at a bench mark on the engine capacity, subsidize the interest rates, as an incentive.

8.2. Translation of the policy initiative [42]

- Establish a separate permanent board/Directorate of Biofuels strictly for agricultural operations.
- The District – wise agricultural energy requirements be translated, into the extent of crop to be grown.
- Ensure for every 200 ha^{+} of such crop (ex. Jatropha), at least two processing plants be encouraged.
- In a time frame, to develop and make it available the engines to rune on SVO/bio-diesel, based on need, and convenience.
- Additional incentive for dual fuel mode of operation to save vegetable oil for other applications.
- Invite involvement of Local engineering institutions to verify the quality aspects of the fuel by providing infrastructure, to act as a resource centers.
- Necessary training and extension programs be motivated with these centers.
- Ensures rural entrepreneurial/work opportunities, by encouraging small scale industrial activity.
- Put in place the mechanism to deliver energy products available locally, to all the stake holders.
- Transition to bio fuels can be developed based on cropping pattern/site and size specific operations, by measuring the actual energy saved.

- For this exercise state bio fuel boards can engage charted engineering/qualified personnel to make such evaluation once in 3 months.
- Savings on fossil fuels is rewarded, as an incentive to the bio-fuel boards of the respective states by EB's/states.
- The CDM cash credits/rewards can be distributed, among the stakeholders as a support price for the raw material/to the distribution mechanism.

8.3. Bio-diesel policy [43]

Beginning 1 January 2006, the public sector OMCs (oil marketing companies) will be purchasing bio-diesel (B100) at Rs. 25 a liter for blending with diesel (HSD) to the extent of 20% in phases. Unveiling the new bio-diesel purchase policy on 13 October, the former minister for petroleum and natural Gas, Mr. Mani Shankar Aiyar, said that to start with, five percent of bio-diesel a non-edible oil extracted from Jatropha and Pungamia, would be mixed with diesel during trial runs. At a later stage, in phases, the B100 blending with diesel is to be increased to 20%. Mr. Alyar noted that automobile engines would not require any modification for using diesel doped with 20% bio-diesel as fuel. Only those bio-diesel manufacturers who get their samples approved and certified by the oil companies, and get registered as authorized suppliers will be eligible for assured purchase of product, the new policy statement said. Accordingly starting 1 January 2006, the OMCs – IOC, BPCL, and HPCL – would purchase through select purchase centers, bio-diesel that meets the fuel quality standards prescribed by the bureau of industrial standards.

9. Environmental considerations

In view of environmental considerations, bio-diesel is considered Carbon neutral because all the CO_2 released during consumption had been sequestered from the atmosphere for the growth of vegetable oil crops. The combustion of bio-diesel has reported to emit lesser pollutants compared to diesel [39]. This indicates that the engine exhaust contains no SO2, and shows decreasing emissions of PAH, CO, HC, soot and aromatics. The NO_x emission is reported to be in the range between $\pm 10\%$ as compared to diesel depending on engines combustion characteristics.

10. Economic feasibility of bio-diesel

India has rich and abundant resources of edible and non-edible oil seeds, the production of which can be stepped up manifolds if the government provides incentives to farmers for production of bio-diesel. The economic feasibility of bio-diesel depends on the price of crude petroleum and the cost of transporting diesel over long distances to remote areas. It is a fact that the cost of diesel will increase in future owing to the increase in its demand and limited supply. Further, the strict regulations on the aromatic and Sulphur contents of diesel fuel will make diesel costlier. Similarly, reducing the sulphur content is also a big challenge for the industries currently; the production of methyl or ethyl esters from edible oil is much more expensive than that of diesel fuels due to the relatively high costs of vegetable oils. The cost can be reduced further if we consider non-edible oils, used frying oils and acid oils instead of edible oils. Non-edible oils from the sources such as neem, mahua, pongamia, karanji, babassu, jatropha, etc., are easily available in many parts of the world including India, and are very cheap compared to edible oils [44,45].

11. Conclusion

Alternate fuels for diesel engines have become increasingly important due to decreasing petroleum resource and environmental consequences of exhaust-gases from petroleum-fuelled engines. A number of studies have shown that triglycerides hold promise as alternative fuels for diesel engines. However, the high viscosity, low volatility and poor cold flow properties of triglycerides, which result in severe engine deposits, injector choking and piston ring sticking have prevented triglycerides from being used directly in diesel engine. Various blends of bio-diesel with diesel have been tried, but B-20 has been found to be the most appropriate blend. The quality of bio-diesel is most important for engine part of view and various standards have been specified to check the quality. As per the analytical method reported in literature high performance liquid chromatography method is suitable to analyze the reaction intermediates and products of transesterification reaction. Economic feasibility study shows that the bio-diesel obtained from non-edible oil is cheaper than that from edible oils.

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